INHIBITOR RANKINGS FOR ALKANE COMBUSTION

by

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Reprinted from the Combustion and Flame, Vol. 123, Vol. 4, 488-506, December 2000.

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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The effect of hydrocarbon fuel type on the ranking of inhibitor effectiveness has been investigated through computer simulations. The approach involves carrying out sensitivity analysis on the detailed kinetics of the combustion of C_1-C_4 hydrocarbons. It is demonstrated that the main reactions determining burning velocities are the same. Similar suppressant rankings from the combustion of different hydrocarbon fuels are largely due to the reactions of a number of small radicals that are common to all of these systems. Inhibitor addition reduces the concentration of these radicals with the active agents being recycled by the common breakdown products of the fuel. Inhibitor effectiveness of additives in a variety of fuels was analyzed using experimental data on the effects of additives on burning velocity in small additive concentration ranges. An universal ranking of additive efficiency is presented. The results demonstrate that the active agents in practically all cases are the small inorganic compounds created from decomposition processes. Inhibition effectiveness of agents is at a maximum at low concentrations. At higher concentrations, saturation effects, brought about by the approach of active radicals to their equilibrium concentrations, lead to substantial decreases in the effectiveness of high efficiency suppressants in comparison with their effects at small concentrations. The results show that the probable maximum increase in total flame suppression effectiveness of high efficiency agents will not exceed one order of magnitude in molar fractions in comparison with the effect of halon 1301 (CF_3Br).

INTRODUCTION

Simulation studies on the ranking of the relative effectiveness of fire suppressants have generally focused on the effect of chemical agents on one-carbon fuels such as methane. A typical fuel for cup burner tests is n-heptane. Two important issues must therefore be considered:

(1) Is it possible to represent the combustion properties of different hydrocarbons by a "single" fuel, n-heptane, or by some other hydrocarbon?
(2) Will the suppressant ranking obtained for n-heptane correspond to inhibitor rankings from another hydrocarbon?

There has been very little discussion in the literature on these issues. It is generally accepted that the results of tests on suppressant effectiveness for one fuel will approximate those from other fuels. In this paper we wish to examine the basis for these assumptions and present results that support them in a more definitive fashion.

The paper begins with a brief discussion of the available data on these questions and summarizes the more general mechanistic and experimental information dealing with the similarities in hydrocarbon combustion systems. The main bulk of the study contains results from simulation studies on the combustion of a number of hydrocarbon fuels (alkanes) with or without suppressants. The strategy is to determine the sensitivity of the laminar flame velocity to the specific chemical reactions in the database that is used in the simulations. The work is divided into four parts. The first is concerned with combustion mechanisms without suppressants. The second deals with the effect of Halon 1301 (CF_3Br). A third section discusses the effect of other suppressants. The final section deals with extinction behavior. The results, although not completely surprising, do give a semiquantitative picture of the transferability of suppressant effectiveness data for various hydrocarbon fuels.

BACKGROUND

Two important characteristics of the effect of chemical agents on flame properties are: (i) the ordering of agents according to their suppressant effectiveness and (ii) absolute data expressed in terms of extinction concentrations or agent concentrations required for the same

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0010-2180/00/$–see front matter
PII S0010-2180(00)00168-1

Published by Elsevier Science Inc.

TABLE 1

Properties of Some Stoichiometric Flames

Fuel	Burning velocity, (cm/s)	T_{ad} K	H_{max}	OH_{max}	O_{max}
Methane	43	2226	8.3×10^{-3}	8.3×10^{-3}	4.4×10^{-3}
Ethane	50	2260	10^{-2}	$> 9 \times 10^{-3}$	6.2×10^{-3}
Propane	49	2267	1.15×10^{-2}	$> 9 \times 10^{-3}$	6.6×10^{-3}
Butane	44	2266	1.3×10^{-2}	$> 10^{-2}$	6.7×10^{-3}

From Fristrom [3].

decrease of burning velocity. We summarize briefly general ideas regarding the similarities in reaction mechanisms for hydrocarbon fuels and present data demonstrating similar rankings of suppression effectiveness of compounds for different fuels.

Warnatz [1] and Dixon-Lewis [2] have proposed that in hydrocarbon oxidation flames, the dominant reactions are those for chain branching

$$H + O_2 = OH + O \quad (1)$$

and the process that converts CO

$$OH + CO = CO_2 + H \quad (2)$$

The burning velocity is most sensitive to the rate constants of these reactions. In addition, calculations show that the reactions HCO + M = CO + H + M and H + O_2 + M = HO_2 + M are also of key importance. In flames, the hydrocarbon is attacked by the O, H, and OH radicals that are produced in the course of the reaction. The larger alkyl radicals formed in this manner will then decompose to smaller alkyl radicals by fast elimination of alkenes. The rapidity of the decomposition of the larger alkyl radicals is such that the flame oxidation of all higher hydrocarbons centers about the oxidation of the methyl and ethyl radicals [1]. These steps are the rate-controlling processes in the combustion of alkanes and alkenes, and is the reason for similarity of all alkane and alkene flames [1]. Such similarities are reflected in the narrow range of burning velocities, normalized composition profiles of reactants and main products for the combustion of alkane fuels [3]. A consequence is that, flame velocities of alkane flames can be modeled within a factor of two using the pure H_2-O_2-CO mechanism and the rate constants for the initial attack of H, O, and OH on the particular hydrocarbon [1].

Fristrom [3] has shown that alkane hydrocarbon combustion systems have remarkably similar properties. These are summarized in Table 1 [3] and are based on the flame calculations of Warnatz. The burning velocities of C_1-C_8 alkane flames as a function of equivalence ratio agree within 10–15% except for very rich mixture compositions [3, 4]. In flames of comparable burning velocity, the final adiabatic flame temperature and mixture composition profiles, when plotted on a normalized time basis, are very similar [5]. Early flame structure investigators (Kaskan, [6]; Fenimore [7]; Fristrom, [3]) have observed that hydrocarbon flames may be attributed to a family of fuel destruction reactions by H, O, and OH at the lower flame boundary feeding a H_2-CO/O_2 flame. A pool of radicals is formed and the diffusion of these active species leads to their reactions with the fuel. Thus, the main differences between flames of hydrocarbon fuel systems are in the region of initial fuel consumption.

The first extensive experimental studies on the effect of additives as flame suppressants were carried out at Purdue University [8] using n-heptane as a fuel. Counterflow diffusion flame burners were used for measurements of extinction concentrations of a large number of agents in the works of Hamins et al. [9] and Zegers et al. [10]. The procedure employed in New Mexico Engineering Research Institute of the University of New Mexico (Moore et al. [11]) for suppression effectiveness tests was based on cup burner experiments, also with n-heptane. In addition, Tapscott has gathered and evaluated cup burner data for a variety of fire suppression agents and fuels [12]. Most

TABLE 2

Ordering of Suppressant Efficiency with Various Fuels Based on Burning Velocity

Fuel	Inhibitor Ordering	Reference
Methane	$CF_2Br_2 > Br_2 > CF_3Br > CH_3Br > CH_3I$, $CCl_4 > Cl_2 > CH_3Cl$	[13, 14]
Propane	$CH_2ClBr > CH_3Br > CH_3I > CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl > HCl > H_2O$	[15]
Hexane	$CCl_4 > CHCl_3 > Cl_2 > CO_2$	[16]

kinetic modeling and many experimental studies of inhibition and suppression by chemical agents are mostly concerned with methane-air combustion. We now present some of the experimental data that cover other fuels.

Table 2 contains results of studies on the relative effectiveness of additives on the burning velocity of propane, hexane, and methane flames on the basis of 10–30% decreases in burning velocity. It can be seen that the ordering of suppressant efficiency is the same for three fuels. Other, more exotic suppressants, for example BBr_3, PCl_3 in hexane (Lask et al. [16]) and methane (Rosser et al. [14]), and $Fe(CO)_5$ for methane (Bonne et al. [17]) and hexane (Lask et al. [16]) tend to behave in a similar manner.

An alternative approach to ranking of suppressant effectiveness is to determine the concentration required for extinction. The data are summarized in Table 3. Here again it can be seen that on a relative basis the ordering is the same for the different fuels. Table 4 demonstrates approximately equal extinction concentrations of agents for the combustion of different fuels. In spite of the scatter of the experimental data, extinction concentrations of different agents for alkane combustion, for example for methane and propane, agree within a factor of 2.

Hamins et al. [9] tested eleven agents ($CF_3CH_2CF_3$, $CHFClCF_3$, CHF_2CF_3, C_3HF_7, C_3F_8, CHF_2Cl, CH_2FCF_3, C_4F_{10}, CH_2F_2/CHF_2CF_3(60/40), cyclo-C_4F_8, C_2F_6, CF_3Br). The fuels were heptane in the counterflow configuration, and heptane, the jet fuels JP-8 and JP-5, and hydraulic fluids in the coflowing configuration (cup burner). The oxidizing gas was a mixture of air and the agent. The relative rankings of the effectiveness of various agents agree despite variations in fuel type.

Recently, Zegers et al. [10] tested four fluorinated ethanes, ten fluorinated propanes, four bromine- and iodine-containing halons, and the inert agents CF_4, SF_6, and N_2 as suppressants in methane-air and propane-air nonpremixed counterflow flames, and n-heptane and methanol cup burner flames. Extinction concentrations, within a scatter of 20%, for methane and propane in nonpremixed counterflow flames at a strain rate of 60 s^{-1} are similar to those for n-heptane cup burner flames. The effectiveness ranking of the agents tested was found to be essentially independent of fuel type. Finally, propane and methane flames yield extinction concentrations that are similar to n-heptane values.

This insensitivity to fuel types is not surprising, given that essentially the same active radicals are present for all hydrocarbon fuels. Flame inhibition is generally considered to be a consequence of the competition of the inhibitor species reactions, removing active radicals, with the chain-branching reaction $H + O_2 = OH + O$ that creates them [30–33]. In addition, effective inhibitors must also be able to regenerate the inhibitor agent.

Analysis of inhibition cycles for different effective chemical inhibitors, iron pentacarbonyl [34], phosphorus-containing compounds [35,

TABLE 3

Ranking of Agents According to Suppression Concentrations

Methane	$NaHCO_3$ [18] > Br_2 [19] > CF_3Br [20] > C_4F_{10} [21] > CF_3CHFCF_3 [22] > CHF_3 [23]
Propane	$C_2F_4Br_2$ [24] > CF_3Br [25] > C_4F_{10} [25] > CF_3CHFCF_3 [25] > CHF_3 [25]
n-heptane	$NaHCO_3$ [9] > $C_2F_4Br_2$ [26] > CF_3Br [27] > C_4F_{10} [25] > CF_3CHFCF_3 [9] > CHF_3 [9]

TABLE 4

Extinction Concentrations of Compounds

Inhibitor	Extinction Concentrations of Additive for Stoichiometric Fuel Mixtures (mole fractions, %)	Reference
$KHCO_3$	Methane 0.57	[18]
	n-heptane 0.78	[28]
$NaHCO_3$	Methane 0.33–1.9	[18]
	Methane 1.2	[29]
	n-heptane 1.06	[9]
CF_3CHFCF_3	Methane 8.0	[22]
	Heptane 7.7	[22]
	Propane 11.6	[22]
	i-butane 11.3	[22]
	Pentane 11.6	[22]
CF_3Br	Methane 4	[20]
	Methane 6.2	[23]
	Heptane 3.1	[27]
	Heptane 2.9–4.0	[25]
	Propane 7.6	[23]
	Propane 4.3–7.7	[25]
Br_2	Methane 2.5	[19]
	nC_6H_{14} 2.3	[18]

36], compounds containing K, Na [37, 38], Br, I [39, 40], shows that the experimental results are explicable without recourse to reactions specific for a particular hydrocarbon fuel. The kinetic models demonstrate that inhibition occurs with the same set of inhibitor species and independent of the fuel. For example, in the case of brominated suppressants, the active agents are HBr and Br, with some contributions from C_2H_3Br, CH_3Br, and C_2H_5Br. For fluorinated hydrocarbon compounds (HFCs), the suppression effect is the result of scavenging reactions of products from the consecutive degradation of fluorinated compounds (Westmoreland et al. [41]; Noto et al. [42]). They are nonspecific with respect to the type of fuel.

Our previous modeling studies [40, 42] of inhibition of methane, methanol, ethane, and ethylene flames by CF_3Br, CF_3I, CF_3H, C_2F_6, C_2HF_5, and CF_4 additives show that there exists a strong correlation between the influence of additives on burning velocity and the maximum concentrations of chain carriers. The results on the reduction of H atom concentration are compatible with the rank ordering based on flame velocity decreases. Results for OH and O are similar to those for H atom concentrations. The rank ordering is CF_3Br, $CF_3I > C_2F_6 > C_2HF_5 > CHF_3 > CF_4$, irrespective of the hydrocarbon-air flames studied.

In addition to chemical effects, additives can also influence the thermal characteristics of a flame. The physical influences include heat capacity and dilution effects. Since to a large extent these depend on additive properties alone, it is clear that the contributions due to thermal influences on the relative effectiveness of compounds will be independent of the fuel type. Indeed, the main effect for such agents (inert gases, etc.) is the decrease of flame temperature.

In this paper we examine the basis of the assumption that the inhibitor rankings obtained for different alkane hydrocarbon fuels are similar. The general conclusion that can be drawn from the above considerations is that, for inhibition effects to be influenced by a particular fuel, there must be specific interactions of suppressants with the fuel itself or some early breakdown products that are characteristic of the fuel. In the subsequent sections we attempt to define the chemistry related to suppressant ranking for the combustion of different hydrocarbons through sensitivity analysis. This will determine in an unambiguous and quantitative manner the reactions responsible for combustion and inhibition. Although the studies cover only alkane fuels, the nature of the reaction mechanism is such that they are probably applicable to other type of hydrocarbon fuels. A discussion of this issue can be found in the final section.

KINETIC MODELS. CALCULATIONAL PROCEDURE

Simulations were carried out for methane, ethane, propane, butane, isobutane, and n-heptane flames. The Chemkin suite of programs was used [43]. The first-order sensitivity coefficients of the burning velocity with respect to reaction rates were calculated [43]. The basic kinetic model was that of C_1-C_2 hydrocarbon combustion, previously used in our studies [40]. To describe the combustion of propane and butane, the block of reactions containing C_3-C_4 compounds from the model of Marinov et al.

[44, 45] was added to the database. For isobutane chemistry, an additional block of reactions based on the work of Tsang [46] was incorporated. For the description of the kinetics of isobutene ($isoC_4H_8$) and $isoC_4H_7$ radical we use the suggestions of Wang et al. [47]. To model combustion of n-heptane, a block of reactions from the model of Wang et al. [47] was added to the butane oxidation model.

The merger of the various models (Marinov et al. [44, 45] and Noto et al. [40]) was made so that the present results are compatible with our previous simulations. The difference between the two models with respect to the C_1 and C_2 chemistry is primarily from the inclusion of CHOH and HC(O)OH in Marinov's model. We, along with others (Pereira et al. [48], Held and Dryer [49], Marinov [50]) have found that the reactions of these species do not contribute significantly to the phenomena of interest. The reactions of the additives [CF_3Br, iron pentacarbonyl and dimethylmethylphosphonate (DMMP)] were taken from earlier publications [34, 36, 40].

RESULTS AND DISCUSSION

Mechanisms of Hydrocarbon Combustion (Alkanes)

The basis of the present work is the burning velocities of a fuel/air mixture with and without inhibitor addition. Typical results can be seen in Fig. 1 where we show calculations with CF_3Br, $Fe(CO)_5$,and N_2 as additives. The characteristic feature is the monotonic decrease in flame velocity as the inhibitor concentration is increased.

Direct Effects

Figures 2–6 contain sensitivity coefficients for the burning velocity of different hydrocarbons to the rate constants of reactions. We have arbitrarily set a lower limit of 2% in comparison to that for the main chain-branching process, $H + O_2 = OH + O$ (1). Note that in the subsequent text all comparisons of sensitivity on a relative basis will be with this reaction. Even the most cursory analysis of the data shows that the burning velocity of the various C_1-C_4 alkanes is most sensitive to the same set of reactions. It can be seen that the number of reactions with sensitivity levels more than 10% of that for the main chain-branching process is very small. The important reactions determining burning velocity are thus:

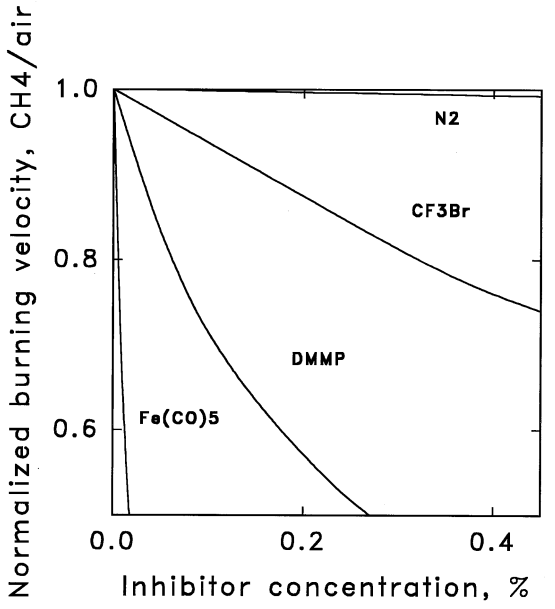

Fig. 1. Dependence of flame velocity on suppressant concentration for some representative additives.

$$H + O_2 = OH + O$$

$$CO + OH = CO_2 + H$$

$$HCO + M = CO + H + M$$

$$H + O_2 + M = HO_2 + M$$

For ethane combustion the reactions,

$$C_2H_5 + H = CH_3 + CH_3$$

$$C_2H_5 + M = C_2H_4 + H + M$$

contribute more than 10% to the sensitivity of burning velocity in comparison to the main chain-branching process. For methane the burning velocity is also sensitive to the reactions

$$H + CH_4 = CH_3 + H_2$$

$$CH_3 + H + M = CH_4 + M$$

For propane there are no reactions that effect the burning velocity to the extent of the reac-

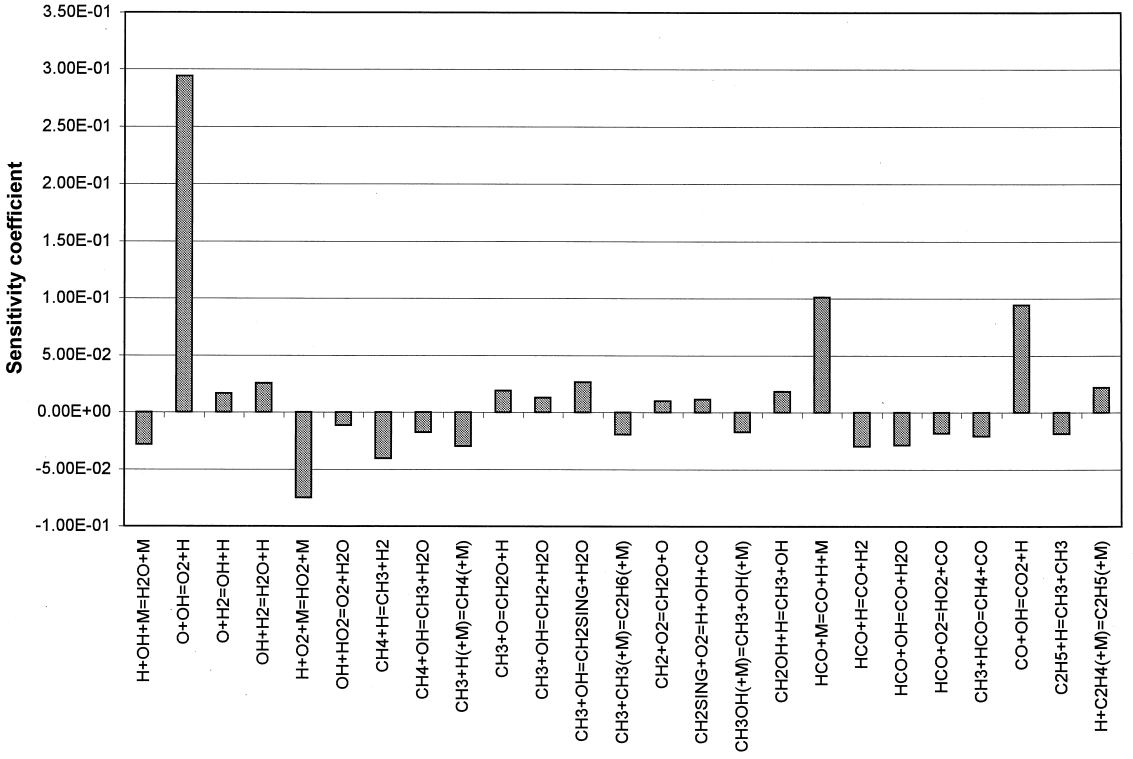

Fig. 2. Relative burning velocity sensitivity coefficients for methane-air flame (stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented.

tions listed above for ethane and methane. Some of the important reactions that contribute to the sensitivity of burning velocity are

$$aC_3H_5 \text{ (allyl)} + H = C_3H_6$$

$$C_3H_6 + H = aC_3H_5 \text{ (allyl)} + H$$

$$C_3H_6 + O = CH_3CHCO + H + H$$

$$iC_3H_7 + H = C_2H_5 + CH_3$$

With n-butane combustion, the abstraction reactions,

$$C_4H_{10} + H = sC_4H_9 + H_2$$

$$C_4H_{10} + OH = sC_4H_9 + H_2O$$

influence the burning velocity at the 3–5% level in comparison to that of the main chain-branching reaction. For the combustion of isobutane, reactions of formation and consumption of i-C_4H_8 and i-C_4H_7 species are most important. However, the sensitivity analysis demonstrates that the sensitivity to the rate constants involving these reactions is less than 10% of the main chain-branching process.

Another approach for assessing the relative influence of rate constants on the flame velocity is to note the consequences on the latter from changes in the former. Table 5 contains results of calculations where the rate constant (k_1) of the most sensitive reaction, $H + O_2 = OH + O$, has been changed by a factor of 2. It can be seen that this leads to changes in the flame velocity of 20–30%. Note that except for methane this change is fairly constant for all the fuels.

These results are extended to the other reactions in the process and are summarized in Fig. 7. We have normalized the data in terms of those for the main chain-branching process, $H + O_2 = OH + O$ (sensitivity coefficient and decrease in flame velocity). The results are based on a factor of 2 change in the rate constants for a stoichiometric butane-air flame and are restricted to those reactions with sensitivity coefficients greater than 4%. It is of interest that relative decreases of the burning velocity and the relative sensitivity coefficients are approximately equal for most of the reactions, in spite of the use of local sensitivity

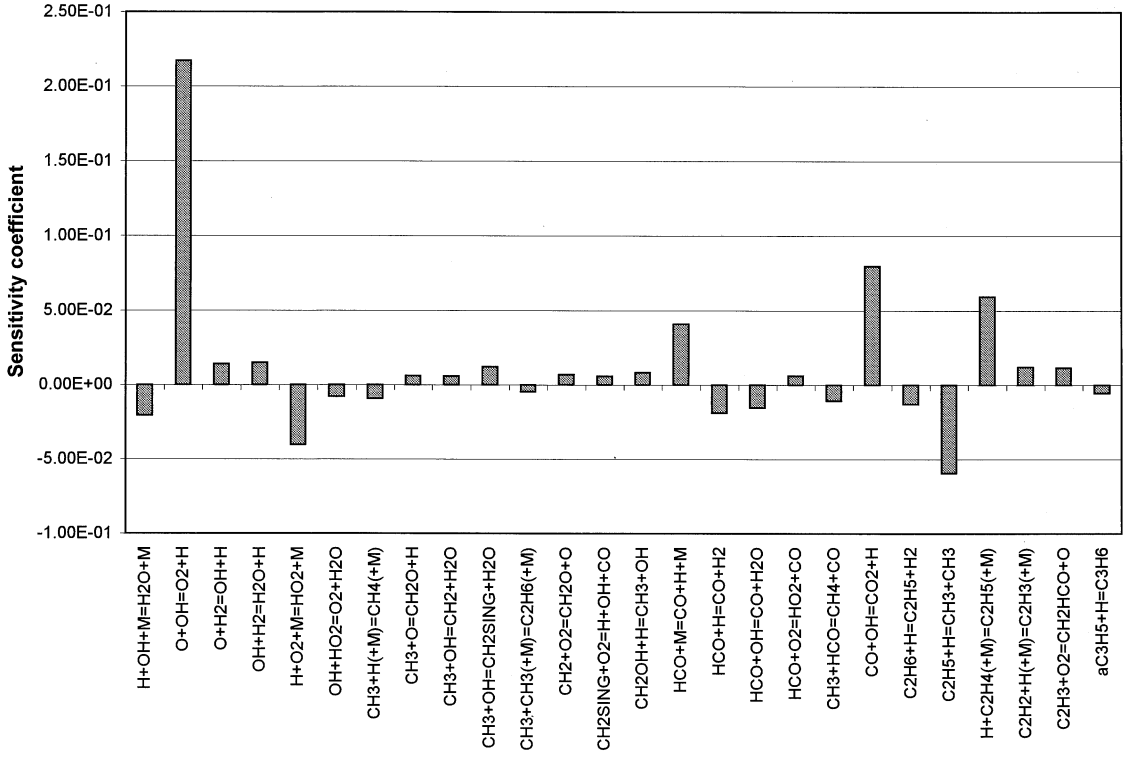

Fig. 3. Relative burning velocity sensitivity coefficients for ethane-air flame (stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented.

coefficient analysis, which is strictly correct only for small changes in the rate constants. In addition, the calculations have also been extended to rate constants of reactions with sensitivity coefficients as low as 0.1% of that for main chain-branching process with very similar results.

Cooperative Effects

The sensitivity coefficients given in Figs. 2–6 define the effect of a change in one of the rate constants on the flame velocity. We next consider cooperative effects or the consequences on the flame velocity brought about by groups of reactions. From Figs. 2–6 it can be seen that there are many reactions with relatively small sensitivity coefficients. The issue is then whether the consequences on flame velocity of all of these reactions with small sensitivity coefficients may in fact be as large as that of the few reactions with large sensitivity coefficients. Simulations were carried out to test this premise using a stoichiometric butane mixture. The simultaneous variations of rate constants were performed for groups of reactions involving C_1-C_2 and C_3-C_4 species. The tested reactions have sensitivity coefficients ranging from 2–4% of the coefficient for the chain-branching process. The cases with positive and negative sensitivity coefficients were modeled separately and together. The observed variations involve reducing rate constants by a factor of 2. Results are presented in Table 6 in terms of relative decreases of burning velocity $(U_{no}-U_n)/(U_{no}-U_1)$, where U_{no} is the burning velocity calculated for original model; U_n and U_1 are the burning velocities calculated with decreased rate constants for the group of reactions and chain-branching reaction 1, respectively.

The calculations show that these changes are manifested in effects that are smaller than would be warranted by a direct summation of the consequences of the individual reactions. Simultaneous change of rate constants for reactions with different signs of the sensitivity coefficient leads to cancellation of the effects and thus relatively small overall influence of these

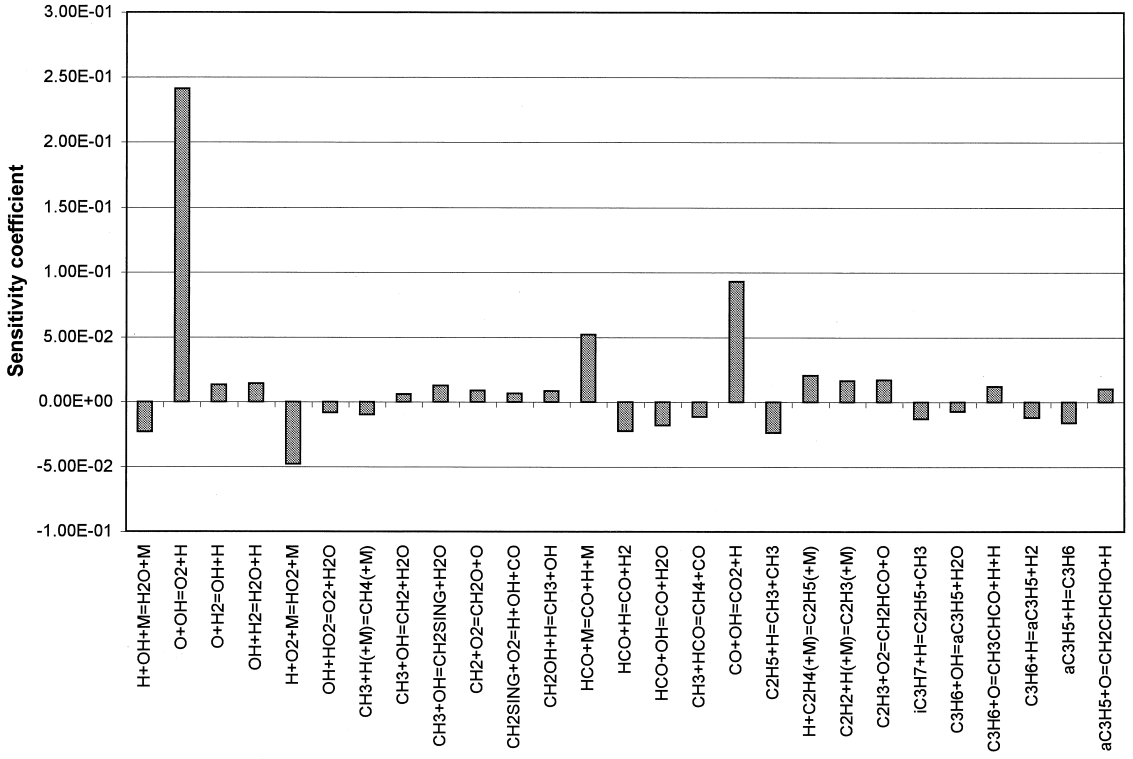

Fig. 4. Relative burning velocity sensitivity coefficients for propane-air flame (stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented.

reactions. Similar results were obtained for propane flame propagation. Overall it can be concluded that the sum of the reactions with small sensitivity coefficients do not lead to effects on flame properties that are larger than that from the main reactions. These results are in line with the conclusions of Brown et al. [51]. On this basis we give in Table 7 a summary list of the reactions with the highest sensitivity in terms of effects on the burning velocity. The cut off has been set at sensitivity coefficients that are no less than 10% of that for the $H + O_2 = OH + O$ reaction. Thus, the reactions that control the flame velocity involve in all cases the breakdown products. Particularly noteworthy is the absence of processes involving propane or butane. On this basis, the calculated results on the similarities in the burning velocity, adiabatic flame temperature, and the concentrations of the key radicals are not surprising (Table 8). These can also be compared with the data given by Fristrom [3] in Table 1.

Influence of Equivalence Ratio

The influence of equivalence ratio is demonstrated in Table 9. Coverage has been restricted to reactions with relative sensitivity coefficients more than 10% of that for the main chain-branching reaction. Lean and rich mixtures of propane and methane were used in the analysis. The number of reactions with relative sensitivity coefficient 10% or larger than that for $H + O_2 = OH + O$ slightly increases with decreasing equivalence ratio. With increasing oxygen content the relative importance of reactions $CO + OH = CO_2 + H$, $HCO + M = H + CO + M$, and $H + O_2 + M = HO_2 + M$ increases. With increasing fuel content, the sensitivity of burning velocity to the rate constant of the main chain-branching reaction $H + O_2 = OH + O$ increases, thus leading to decrease of relative importance of other reactions.

Experimentally, it has been observed (Lask et al. [16]), that the same amount of inhibitor more effective in rich mixtures. This has been

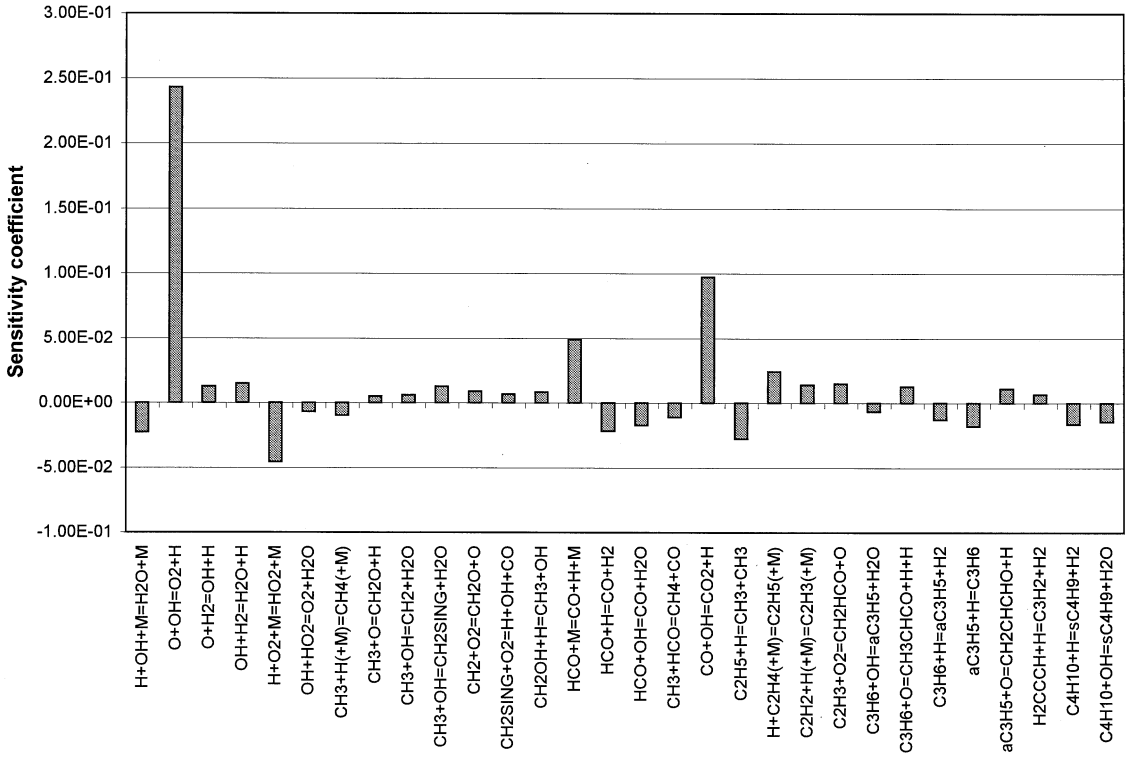

Fig. 5. Relative burning velocity sensitivity coefficients for butane-air flame (stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented.

confirmed in numerical studies (Noto et al. [40]). The slight difference in inhibitor influence on lean and rich mixtures may be due to the increasing influence of the reaction $H + O_2 = OH + O$ for rich mixtures. Since this reaction is the chain-branching reaction, it is possible to expect, that with the increase of sensitivity of burning velocity to this reaction the inhibition effect also increases.

Sensitivity Analysis for Systems Containing CF_3Br

We next consider the situation where a typical suppressant is added to a reaction mixture. For this purpose it is most convenient to consider Halon 1301, CF_3Br, since the database pertinent to its reactions is probably the most reliable. The uncertain issue is the contribution of the inhibitor to reactions involving the parent fuel. If these were important it would lend a degree of specificity to tests with different fuels. In cases where the suppressant acts at sufficiently low concentrations, such reactions would be dwarfed by the overall combustion reactions. For the present situation, we consider the situation where Halon 1301 was added to methane, ethane, and propane flames.

Figures 8 and 9 are the results from the sensitivity analysis. It can be seen that the picture is very similar to that given in the earlier figures for the situation without suppressant. This is indicative of the fact that the overall mechanism has not changed. Particularly interesting is the nature of the contributions from the species that are traceable to CF_3Br. The key observation is that the most sensitive reactions of CF_3Br or its breakdown products are with the breakdown products of the fuel. The reactions with the fuel itself or the larger fragments do not apparently make any contributions. Therefore, the specificity introduced by the different fuel types is also lost from the point of view of inhibition. The following are the reactions, involving brominated species, with the largest sensitivity coefficients:

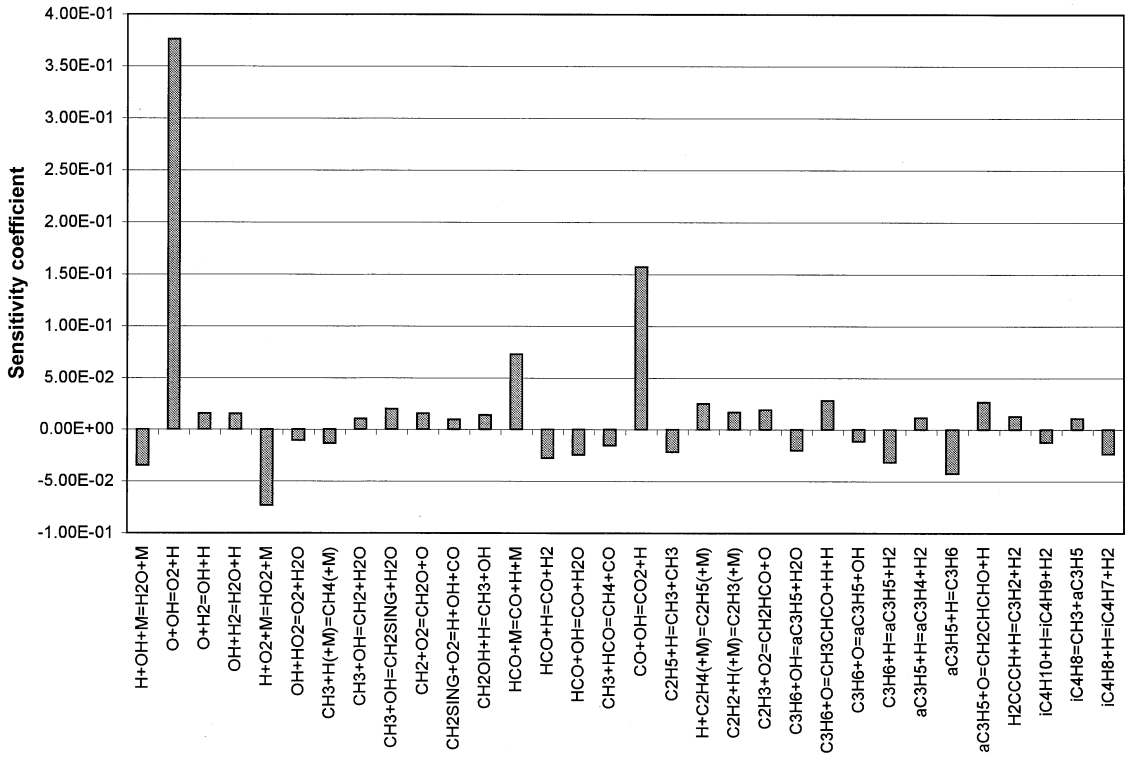

Fig. 6. Relative burning velocity sensitivity coefficients for isobutane-air flame (stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented.

$$Br + HCO = HBr + CO$$

$$H + HBr = H_2 + Br$$

$$H + CF_3Br = HBr + CF_3$$

$$Br + Br + M = Br_2 + M$$

As expected, they are all negative since these are the important reactions in the inhibition cycle. It is interesting that the larger sensitivity coefficient corresponds to the reaction Br + HCO = HBr + CO, and relatively smaller sensitivity is observed for the much better known scavenging reaction H + HBr = H_2 + Br. The CF_3Br effect on flame propagation was studied earlier by Westbrook [32] and Noto et al. [40, 42]. The sensitivity analysis results from this study show the same set of important reactions [32, 40, 42].

TABLE 5

Hydrocarbon	Decrease of Burning Velocity for the Rate Constant $k_1/2$ (%)	Increase of Burning Velocity for the Rate Constant $k_1 \times 2$ (%)
Methane	29	31
Ethane	23	—
Propane	24	—
Butane	23	—
Heptane	23	—

Simulations with different concentrations of the suppressant (0.3–2%) demonstrate that pattern of sensitivity coefficients for reactions of hydrocarbon oxidation remains practically the same with approximately the same sensitivity coefficients for the main reactions. This can be seen in Fig. 10. As expected, increasing additive concentrations are directly manifested in the increasing sensitivity to the set of inhibitor reactions given above. Thus, the sensitivity coefficient with respect to the flame velocity for the reaction Br + HCO = HBr + CO increases from 12.5% at 0.3% of additive to 42% at 2%, while that of the combination process Br + Br + M = Br_2 + M increases from 0.14% at 0.3%CF_3Br to 17% at 2% of CF_3Br (stoichio-

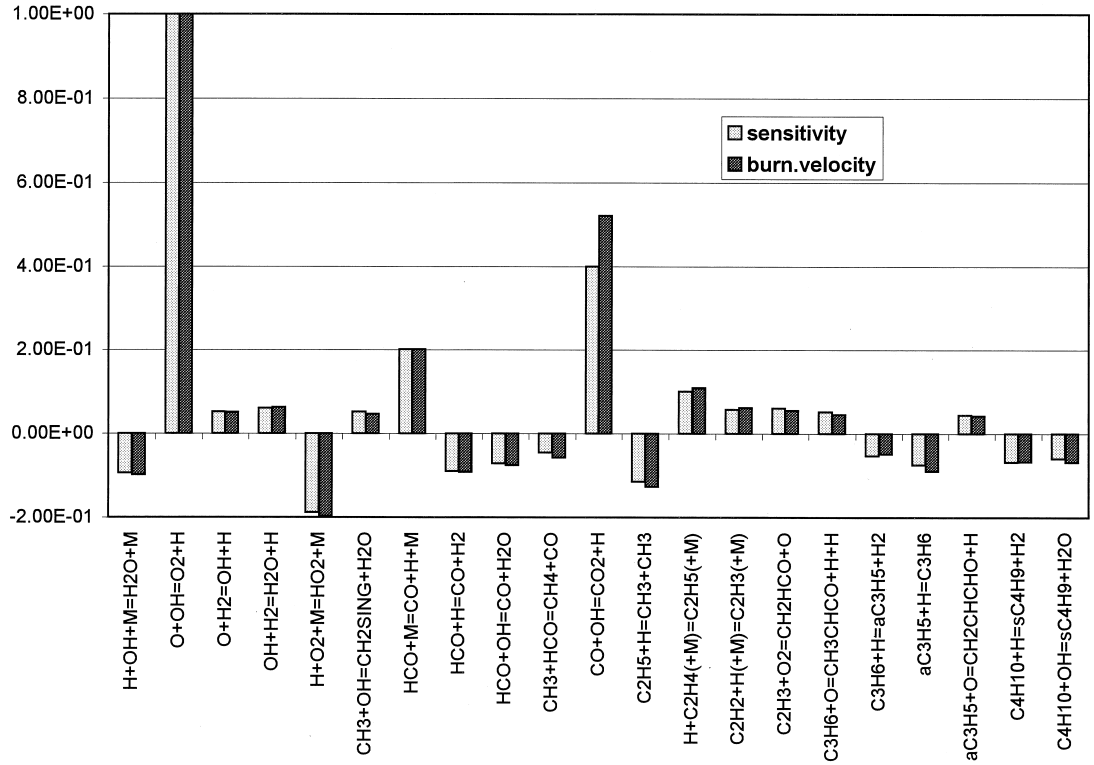

Fig. 7. Comparison of sensitivity coefficients and normalized responses of burning velocity for stoichiometric butane-air flame. Reactions with the level more than 4% of a corresponding value for chain-branching reaction 1 are presented.

metric methane-air flame). The large variation of the sensitivity coefficient for the recombination reaction Br + Br + M is to be expected. The rate of this process has a second-order dependence on the bromine concentration. Note that an increase in concentration from 0.3% to 2.0% of CF_3Br leads to a 3-fold decrease in flame velocity. However the set of reactions responsible for the flame velocity has not been altered. Only their relative contributions to the overall phenomena have been changed.

The sensitivity coefficients of the fluorinated compounds (CHFO species) are all small. They can be either negative or positive. This is in line with the consensus opinion that fluorinated

TABLE 6

The Cooperative Effect of Reactions with Small Sensitivity Coefficients

Cooperative effect of reactions of C1-C2 hydrocarbon species	Influence of reactions with positive sensitivity coefficients, 12 reactions	0.16
	Influence of reactions with negative sensitivity coefficients, 10 reactions	0.2
	Overall effect of reactions with positive and negative sensitivity coefficients, 22 reactions	0.047
Cooperative effect of reactions of C3-C4 hydrocarbon species	Influence of reactions with positive sensitivity coefficients, 8 reactions	0.13
	Influence of reactions with negative sensitivity coefficients, 8 reactions	0.115
	Overall effect of reactions with positive and negative sensitivity coefficients, 16 reactions	0.022

TABLE 7

Relative Sensitivity Coefficients of Burning Velocity to Rate Constants of Different Reactions

Reaction	Methane	Ethane	Propane	Butane	Iso-butane
$H + O_2 = OH + O$	1 (0.294)*	1 (0.217)*	1 (0.241)*	1 (0.243)*	1 (0.376)*
$H + O_2 + M = HO_2 + M$	−0.255	−0.186	−0.198	−0.188	−0.194
$H + CH_4 = CH_3 + H_2$	−0.138	—	—	—	—
$CH_3 + H + M = CH_4 + M$	−0.101	—	—	—	—
$HCO + M = H + CO + M$	0.344	0.188	0.216	0.202	0.193
$HCO + H = CO + H_2$	−0.102	−0.088	−0.094	−0.089	−0.073
$CO + OH = CO_2 + H$	0.321	0.367	0.386	0.4	0.42
$C_2H_5 + H = CH_3 + CH_3$	−0.063	−0.273	−0.098	−0.114	−0.057
$H + C_2H_4 + M = C_2H_5 + M$	0.078	0.273	0.085	0.1	0.067
$aC_3H_5 + H = C_3H_6$		−0.025	−0.066	−0.074	0.11

* The value of sensitivity coefficient for $H + O_2 = OH + O$ reaction is presented in parentheses for corresponding hydrocarbon flames.

compounds by themselves are not effective suppressants. Increasing CF_3Br concentration leads to increases in sensitivity coefficients for the reactions with fluorinated species. However, they still remain small in comparison with contributions from reactions with bromine-containing inhibitor species.

Reaction pathway analysis reveals several additional reactions of importance in the inhibition cycles for methane and propane flame with CF_3Br as the suppressant: $Br + CH_2O = HBr + HCO$, $Br + C_2H_3 = C_2H_3Br$, $H + C_2H_3Br = HBr + C_2H_3$, $Br + CH_4 = HBr + CH_3$, $Br + C_3H_8 = HBr + nC_3H_7$. Particularly interesting are the contributions from the last two reactions. At first glance the contributions from such reactions are surprising, since these are much more endothermic than the reactions of radicals such as OH, H, and O. However the relative inertness of the bromine compounds means that the concentrations are high. This compensates for the smaller value of rate constants. In the present context, these are the types of reaction that may make suppressant effectiveness sensitive to fuel type. Their sensitivity coefficients are, however, small. A closer examination reveals the reason. For every reactive CH_3 formed, a scavenging molecule HBr is also created. Furthermore, the HBr would be formed in any case by some of the other reaction channels. The consequence is that in these cases the contributions from reaction with the fuel molecules considered here are relatively unimportant for suppressant effects.

Extinction Behavior

Chemical influences on fire suppression are most pronounced at low concentrations. However, as the concentration of suppressant is increased, a saturation effect occurs [40, 34]. The general phenomenon is illustrated in Fig. 1. This decrease in chemical effects means that near extinction, contributions from heat capac-

TABLE 8

Properties of Stoichiometric Alkane Flames

Fuel	Burning Velocity (cm/s)	T_{ad} (K)	H_{max} (mole fraction)	OH_{max} (mole fraction)	O_{max} (mole fraction)
Methane	41.4	2238	7.1×10^{-3}	7.8×10^{-3}	3.4×10^{-3}
Ethane	45.8	2276	8.7×10^{-3}	8.2×10^{-3}	4.4×10^{-3}
Propane	44.1	2289	9×10^{-3}	8.1×10^{-3}	4.5×10^{-3}
Butane	43.2	2289	8.9×10^{-3}	8×10^{-3}	4.5×10^{-3}
Isobutane	39.8	2289	8.4×10^{-3}	7.9×10^{-3}	4.3×10^{-3}
Heptane	43.1	2298	8.8×10^{-3}	8×10^{-3}	4.6×10^{-3}

TABLE 9

Influence of Equivalence Ratio

Reaction	Methane, Equivalence Ratio			Propane, Equivalence Ratio		
	0.7	1	1.2	0.7	1	1.2
$H + O_2 = OH + O$	1 (0.318)*	1 (0.291)*	1 (0.314)*	1 (0.214)*	1 (0.241)*	1 (0.269)*
$OH + H_2 = H_2O + H$	0.157	0.087	0.015	0.132	0.0593	—
$H + O_2 + M = HO_2 + M$	−0.717	−0.255	−0.112	−0.565	−0.198	−0.082
$OH + HO_2 = O_2 + H_2O$	−0.118	−0.04	−0.02	−0.118	−0.034	—
$H + HO_2 = OH + OH$	—	—	—	0.108	0.032	—
$H + CH_4 = CH_3 + H_2$	−0.105	−0.138	−0.125	—	—	—
$CH_3 + H + M = CH_4 + M$	−0.075	−0.101	−0.135	—	—	—
$CH_3 + OH = CH_2(s) + H_2O$	0.134	0.09	0.061	—	—	—
$CH_3OH + M = CH_3 + OH + M$	−0.16	−0.059	—	—	—	—
$HCO + M = H + CO + M$	0.541	0.344	0.304	0.321	0.216	0.2
$HCO + H = CO + H_2$	−0.53	−0.102	−0.11	−0.0763	−0.934	−0.11
$HCO + OH = CO + H_2O$	−0.121	−0.097	−0.067	−0.101	−0.075	−0.056
$HCO + O_2 = HO_2 + CO$	−0.31	−0.062	−0.039	−0.106	—	—
$CO + OH = CO_2 + H$	0.79	0.321	0.117	0.93	0.386	0.162
$C_2H_5 + H = CH_3 + CH_3$	−0.043	−0.063	−0.084	−0.079	−0.098	−0.104

* The value of sensitivity coefficient for $H + O_2 = OH + O$ reaction is presented in parentheses for corresponding hydrocarbon flames.

ity and dilution effect become much more important [42]. The decrease in chemical effectiveness demonstrates that the highly efficient inhibitors may not be able to yield extinction by chemical influence only. The cause of this decrease in chemical effect can be attributed to two sources. First the concentrations of the active radicals are driven down to their equilibrium concentrations, and second, in the case of metals, there is the condensation of the active species. The limits for the latter are set by the saturated vapor pressure of the compounds or related compounds responsible for suppression. Thus, it is not possible to linearly extrapolate the results from experiments conducted at low concentrations of suppressant loading, to determine extinction conditions for highly effective chemical suppressants. This is much less true in the cases where purely physical effects are controlling. This may well be the reason for the past controversy over whether physical and chemical effects are responsible for suppression. The analysis suggests that a bifunctional compound may have definite advantages.

It is interesting to estimate the minimum concentration of inhibitor required for flame suppression. The minimum concentration can be estimated using the gas-phase model involving iron pentacarbonyl as suppressant with a premixed methane-air stoichiometric flame. The level of 5 cm/s of burning velocity is accepted as corresponding to flammability limit (Westbrook [32]). Calculations show that the 0.15–0.3% of $Fe(CO)_5$ is required for suppression using assumed rate constants. For comparison the calculated extinction concentration of CF_3Br is 3.5%.

An important consequence of the above is that the differences in suppression effectiveness are much less at higher concentration than at the lower levels where chemistry is most manifest. This sets limits on possible improvement of agent suppression effectiveness in the case of high efficiency compounds, such as those containing Fe, Pb, Cr, K, and Na. They may in fact be no more than an order of magnitude more efficient than CF_3Br. It is, however, interesting that this compression in agent effectiveness when the entire range is considered does not appear to change the ranking of the various agents. Of course, data on this basis is very scarce.

Other Fuels

An interesting issue is the generalization of the results on the lack of dependence of the ranking of inhibitor effectiveness on the nature of the

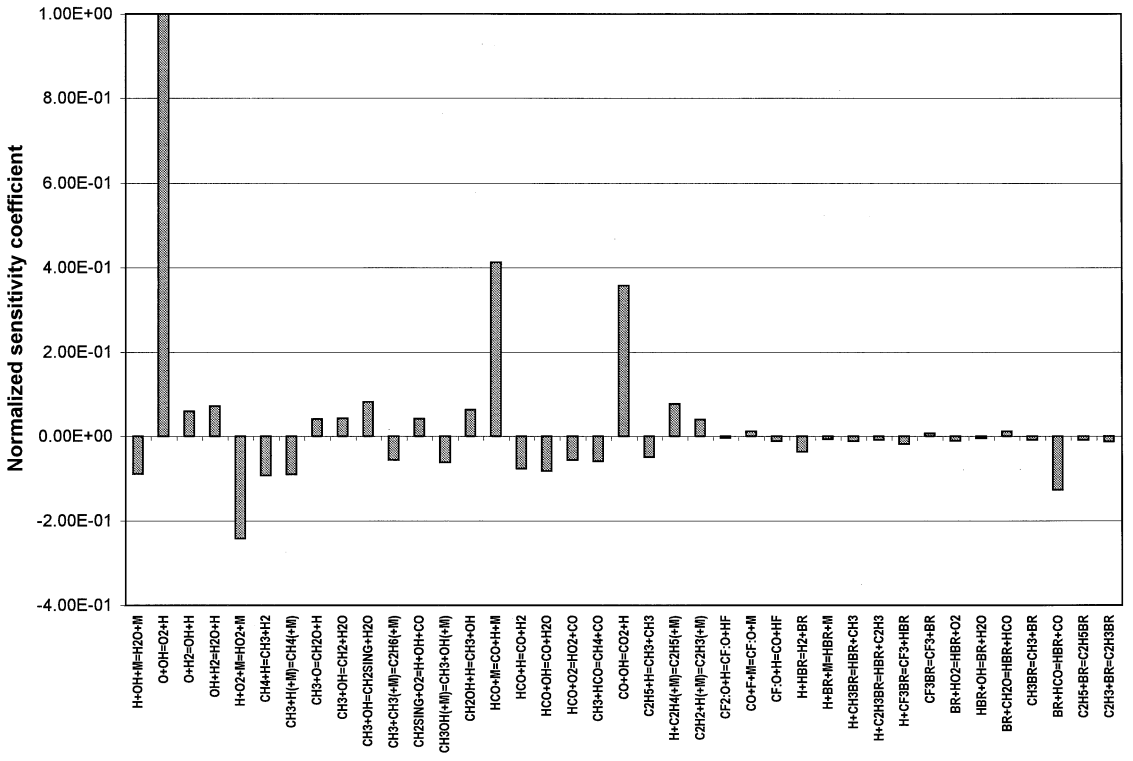

Fig. 8. Relative burning velocity sensitivity coefficients for CF_3Br inhibited methane-air flame (CF_3Br 0.3%, stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented. Reactions with inhibitor species are presented at the level more than 0.4%.

fuel. The compounds discussed here are alkanes. There is no reason why rankings for other fuel types could not be different than those given here. For example, recent studies of the N_2O + CO system show promotion instead of inhibition with the addition of $Fe(CO)_5$ (Linteris et al. [52]). The contributions from the reactions with small sensitivity coefficients, although small, may make a difference. Thus it has been noted that CF_3I is a more effective inhibitor for methanol flames than CF_3Br (Noto et al. [40]).

It may well be worthwhile to draw a distinction between fuel types. Here the observation of Warnatz [1] mentioned earlier is extremely important. Specifically it deals with the instability of alkyl radicals and their rapid decomposition to form small radicals and olefins. Thus, it is highly likely that the present results are also applicable to practically all alkanes regardless of their size. It should be noted that since Beta bond cleavage is even more facile with O and N substitution, it is likely that such substitution would not have important consequences for such compounds. A possible remaining issue is the role of fuels containing aromatic groups. This is probably most uncertain for benzene, since new species must now be introduced. However for alkylated aromatic compounds, one would expect results to follow the general trends with increasing length of the alkyl substitutent. The present analysis gives the rationale for projecting data on relative suppressant effectiveness in one fuel to another and as will be seen subsequently can be extremely useful in rationalizing the large volumes of data that are available.

Other Suppressants

The relative independence of inhibitor effectiveness with respect to alkanes can lead to a universal ranking of additive effectiveness. This is illustrated in Table 10 and Fig. 11 and is derived from a large variety of sources. The rankings were established from measured burn-

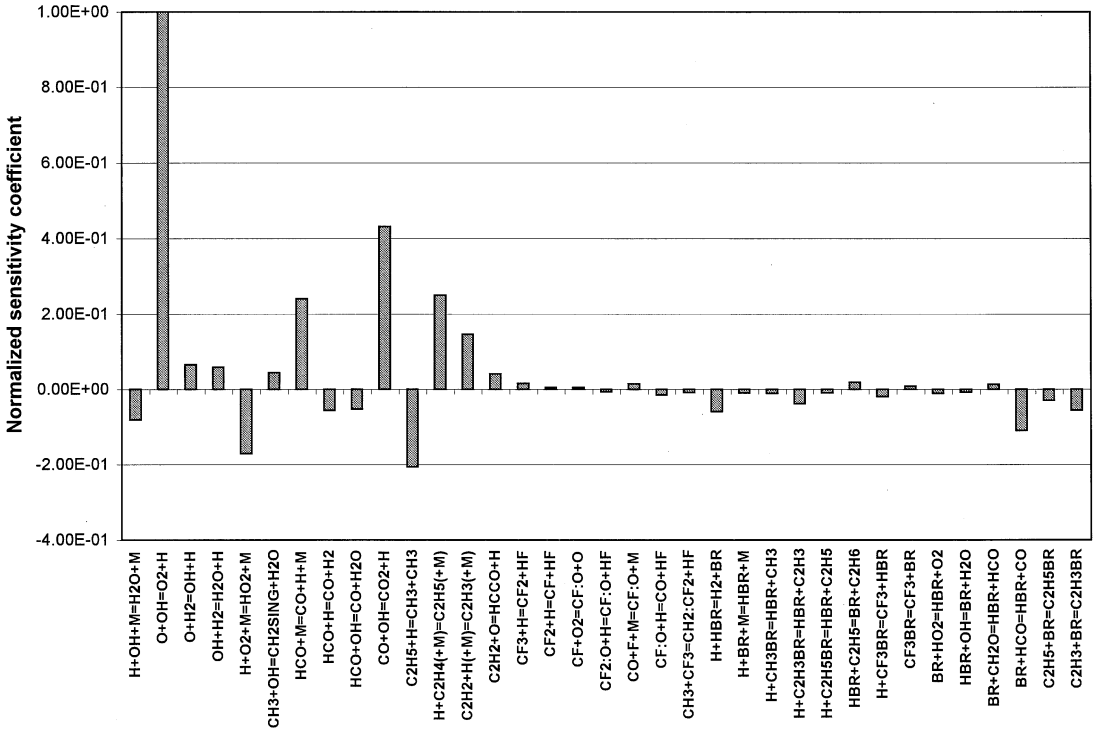

Fig. 9. Relative burning velocity sensitivity coefficients for CF_3Br-inhibited ethane-air flame (CF_3Br 0.5%, stoichiometric mixture, 1 atm). Reactions with sensitivity coefficients more than 2% of sensitivity coefficient for reaction 1 are presented. Reactions with inhibitor species are presented at the level more than 1%.

ing velocity decreases brought about by the addition of inhibitors. It is assumed that there exists a similarity in the influence of inhibitors on different hydrocarbon flames and different equivalence ratios (i.e., ranking and relative influence are the same) as discussed above. The literature data are treated on a molar basis and reduced to a single fuel system (stoichiometric methane-air mixture at ambient conditions) and scaled to a single fuel mixture composition. Data were estimated by using as benchmarks the burning velocities obtained for the same inhibitors in different systems. Where available, the data used were obtained for a relatively small range of additive concentrations and for burning velocity decreases of 10–30%. The compounds considered are mostly liquids or solids and include experiments with fine mists or finely divided powders of inhibitors. Many of the additives in Table 10 are small inorganic compounds. Experimental results obtained for such compounds are also treated on the molar basis. All of the data are based on experimental results in hydrocarbon flames and normalized to the values for CF_3Br.

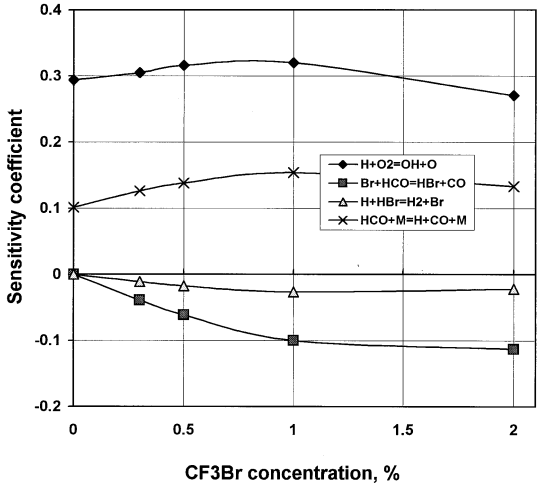

Fig. 10. Burning velocity sensitivity coefficients of methane-air flame as a function of CF_3Br concentration for reactions $H + O_2 = OH + O$, $HCO + M = H + CO + M$, $H + HBr = H_2 + Br$, and $Br + HCO = HBr + CO$.

Table 10 contains data on the number of

TABLE 10

Inhibitor Efficiences of Different Compounds in Small Concentration Range According to Decreases in Burning Velocities

Additive	Molecules of Inhibitor Required per 100 Molecules of CH_4 for 10% Reduction of Burning Velocity	Inhibition Parameter	Coefficient of Efficiency Relative CF_3Br	Reference(s)
CO_2	10	2	0.12	[53]
SO_2	5.7	3.5	0.21	[54]
SF_6	5	4	0.24	[14]
HCl	7.1	2.82	0.17	[15]
CH_3Cl	4.9	4.08	0.24	[53, 15, 13]
Cl_2	3.8	5.26	0.32	[53, 13, 16]
CF_3Cl	3.2	6.25	0.38	[56]
$CHCl_2F$	2.6	7.69	0.46	[56]
CCl_4	1.7	11.8	0.71	[13, 16]
SiF_4	~4.9	4.08	0.25	[57]
$SiHCl_3$	3.5	5.71	0.34	[19]
$Si(CH_3)_4$	1.8	11.1	0.67	[19]
CF_4	~6.5	3.08	0.19	[58, 39, 57]
CHF_3	3	6.67	0.4	[58, 39]
CF_3CHFCF_3	2.8	7.16	0.43	[59]
BF_3	~2	10	0.6	[14]
BCl_3	~2	10	0.6	[14]
BBr_3	~0.29	69	4.1	[16, 14]
CH_3I	1.7	11.8	0.71	[53, 13, 15]
i-C_3H_7I	1.4	14.3	0.86	[13]
HBr	1.8	11.1	0.67	[53, 13]
CH_3Br	1.6	12.5	0.75	[53, 13, 60]
CF_3Br	1.2	16.7	1	[53, 13, 56, 61]
Br_2	0.83	24.1	1.4	[53, 13]
$CHBr_3$	0.51	39.2	2.35	[53]
$SiCl_4$	0.67	29.9	1.8	[19]
$GeCl_4$	0.6	33.3	2	[54, 16]
$AsCl_3$	0.45	44.4	2.7	[19]
$(C_2H_5)_3PO_4$	0.32	62.5	3.75	[19]
$(CH_3)_3PO_4$	0.3	66.7	4	[16]
$SbCl_3$	0.28	71.4	4.3	[19, 57]
$POCl_3$	0.23	87	5.2	[19]
$TiCl_4$	0.22	90.9	5.5	[24, 53, 16]
$SnCl_4$	0.21	95.2	5.7	[16, 19]
$PSBr_3$	0.18	111	6.7	[19, 16]
PCl_3	0.175	114	6.9	[24, 53, 14]
PBr_3	0.175–0.27	114	6.9	[16]
NaCl	~0.16	125	7.5	[62]
$PSCl_3$	0.15	133	8	[16]
CuCl	~0.11	182	10.9	[62]
$NaHCO_3$	0.1	200	12	[62]
K_2SO_4(+Cab-O-Sil)	~0.082	244	14.6	[62, 63]
Na_2CO_3	0.073	274	16.4	[63]
$KHCO_3$	0.05–0.07	286	~17	[63]
CrO_2Cl_2	<0.03	667	>40	[16]
$Pb(C_2H_5)_4$	0.022	909	55	[16]
$Fe(CO)_5$	0.02	1000	60	[19, 16, 64]

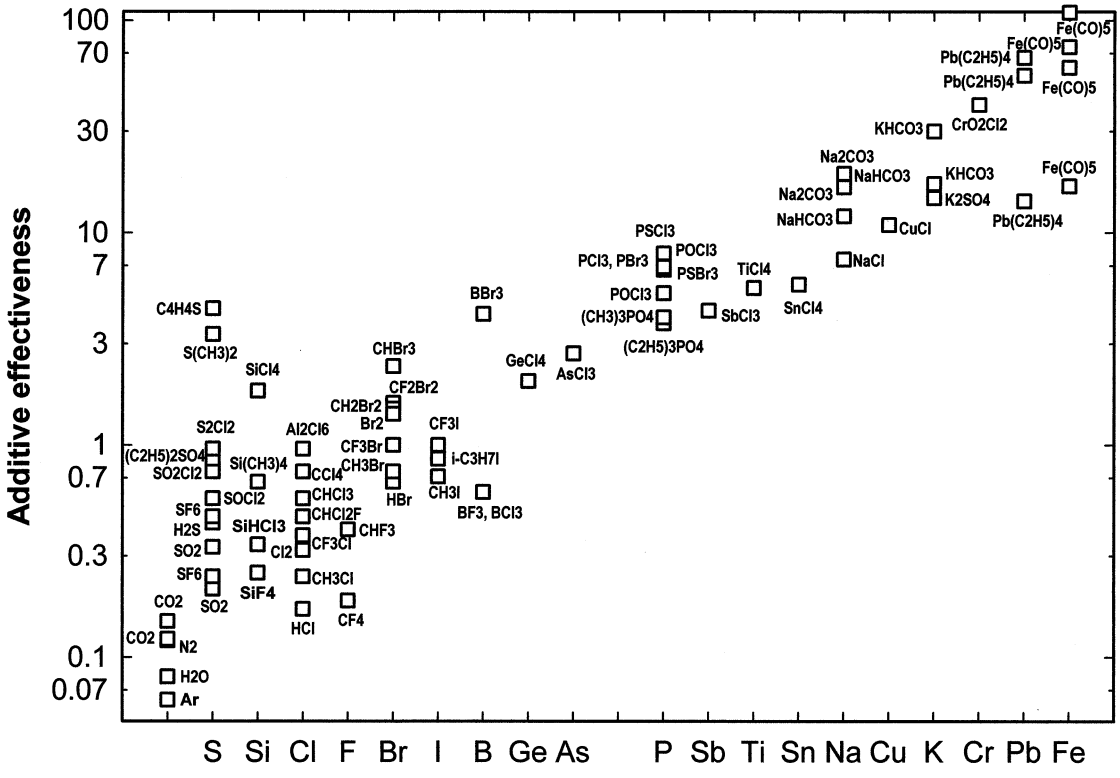

Fig. 11. Relative inhibitor effectiveness. Additive effectiveness is presented in coefficients of efficiency relative CF_3Br.

inhibitor molecules required per 100 molecules of CH_4 for 10% reduction of burning velocity. This measure has been used earlier by Friedman and Levy [65] and Baratov [24]. In addition, the table contains coefficients of efficiency of compounds relative to CF_3Br and inhibition parameters of compounds consistent with the definition of Fristrom and Sawyer [66]. An alternative approach to presenting data can be found in Fig. 11 and is given in the order of increasing inhibitor efficiency.

There are a number of interesting consequences from the data presented in Fig. 11 and Table 10. It is clear that the metallic compounds containing Fe, Pb, and Cr are the most effective. Next in effectiveness are alkali compounds containing Rb, K, and Na. It is possible that compounds of Mn and Sn may be as efficient as the alkali metals. Boron compounds are not effective inhibitors in general. BBr_3 was found to be effective, but this may be due to the presence of bromine. Another interesting result is the grouping together of agents that contain a specific element. This is very strong evidence that the suppressant action is caused by a specific atom or closely related molecule and is relatively independent of the ligands that surround it.

SUMMARY AND CONCLUSIONS

We have applied sensitivity analysis to obtain information on the mechanism of suppressant action on a variety of organic fuels. The analysis of kinetic mechanisms of combustion of C_1-C_4 hydrocarbons demonstrates that the main reactions determining burning velocity are the same for alkane flames. These results demonstrate that similar inhibitor rankings for combustion of different fuels are largely due to the reactions of a number of small radicals that are common to all of these systems. These radical concentrations are reduced through the addition of suppressants. The active agents in the case of these suppressants are likely to be formed or recycled by the breakdown products of the fuel, which are also common to all hydrocarbon fuels. Thus the basic mechanisms for suppressant action in

alkane flames are similar. There is a fairly high likelihood that other types of hydrocarbon flames will have similar attributes. Thus the use of effectiveness rankings from one hydrocarbon fuel to cover other hydrocarbon fuels would appear to be generally justified.

We would like to thank Dr. N. Marinov and Professor P. Dagaut for providing their kinetic models. The authors are grateful to Dr. D. R. Burgess, Dr. W. Grosshandler, and Dr. N. Marinov for helpful discussions. This research is part of the Department of Defense's Next Generation Fire Suppression Technology Program, funded by the DoD Strategic Environmental Research and Development Program.

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Received 4 February 2000, revised 17 May 2000, accepted 20 May 2000